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(54) Title: AQUEOUS COPPER COMPOSITION

(57) Abstract: An aqueous copper composition is provided for use in hydrometallurgical flotation processes comprising a copper component, an ammonium hydroxide component or an amine component, and a weak acid component. The composition is used as an activator in hydrometallurgical flotation processes to activate sphalerite, pyrrhotite, marmatite, and arsenopyrite. The composition replaces copper sulphate and is added in an amount from 20 to 40% (w/w) of the standard amount of copper sulphate generally used as an activator.
TITLE

"AQUEOUS COPPER COMPOSITION"

FIELD OF THE INVENTION

The present invention relates to an aqueous copper composition and in particular to an aqueous copper composition for use in hydrometallurgical flotation processes.

BACKGROUND OF THE INVENTION

Froth flotation processes are widely used to concentrate sulfide minerals, non-sulfide metallic minerals, non-metallic minerals, and coal. The technique can be successfully used to concentrate low-grade ores or ores that must be finely ground to achieve liberation of their values. Flotation is also well suited to the separation and concentration of several minerals found in complex ores, accomplishing separation and concentration with greater accuracy and efficiency than concentration and separation effected by specific gravity methods, for example. Froth flotation is thus very effective for the processing of ores containing mixed sulphides of lead, zinc, copper, and iron, producing a relatively pure concentrate of each sulfide. The principle of flotation is based on the attachment of mineral particles to rising air bubbles in a flotation cell. The air bubbles are then carried to the surface to collect as a froth, which in turn is removed. Theoretically flotation can be applied to any mixture of particles that are essentially free from one another and that are small and light enough to be lifted by the rising air bubbles in the flotation cell. Flotation is a physicochemical method of concentration that involves conditioning, by chemical treatment, of the surface of the mineral particles in an ore pulp to create conditions favourable for the attachment of specific, predetermined mineral particles to air bubbles. The air bubbles rise through a water bath containing the ore pulp in the flotation cell and carry the selected minerals to the surface, where a stabilised froth
forms that is then skimmed off and the mineralised particles in it are recovered. Other minerals and gangue which were not among those predetermined to be attracted to the air bubble remain submerged in the flotation cell tank.

Flotation reagents, to chemically condition the mineral particle surface, are usually mixed in ahead of the flotation cells, thus allowing the chemical reactions to take place in sufficient time before the actual flotation process is commenced. The six types of reagents used are known as frothers, collectors, regulators, activators, depressants and dispersants. They are added in small, carefully controlled amounts to the ore pulp in the conditioning tanks or directly to the flotation cells to selectively coat the mineral particles and make them either more or less hydrophobic.

Activators are chemicals, usually inorganic, which are used to effect the flotation of certain metallic and non-metallic minerals that are difficult or impossible to float with collectors and frothers alone. The activators alter the chemical nature of the mineral surface by placing a film over it which is more hydrophobic than was the unaltered surface condition of the mineral, and by doing so make it more subject to the action of a collector.

Activators are generally soluble salts that release solvated ions to react with the mineral surface. Activators, such as copper sulphate, lead and copper carbonates, sodium sulfide, lead acetate, lead nitrate and sodium silicate are commonly used.

Copper sulphate is used universally for the activation of sphalerite, pyrrhotite, marmatite and arsenopyrite. Copper ion substitution on the mineral surfaces vastly improves their floatability with xanthate collectors. Copper sulphate is added in liquid or dry form, with the preferred method being to prepare a solution of known strength and to add it to the conditioning tank ahead of the flotation cells.
The efficiency of aqueous solutions of copper sulphate, however, is compromised by the precipitation of copper hydroxide when solution pH is greater than 5.0. Consequently the concentration of soluble aqueous copper ions available for hydrometallurgical processes may be reduced to 10% of total concentration.

It is known to provide an aqueous solution of an organic copper complex that is efficiently used as an activator for zinc sulphides such as sphalerite and marmatite, as well as other minerals such as pyrrhotite, cryolite, vanadinite and zircon. Organic copper complexes are also used in the recovery of arsenopyrite, cobalt, arsenides, iron sulphides, stibnite and free gold. Typically, organic copper complexes are soluble in a broader pH range. However, the application of organic copper complexes in hydrometallurgical process has not been broadly adopted because they are not readily available in industrial quantities or at economical prices.

The present invention seeks to overcome at least in part some of the aforementioned disadvantages.

**SUMMARY OF THE INVENTION**

In accordance with a first aspect of the present invention there is provided an aqueous copper composition for use in hydrometallurgical flotation processes comprising a copper component, ammonium hydroxide, and a weak acid component.

In accordance with a second aspect of the present invention, there is provided an aqueous copper composition for use in hydrometallurgical flotation processes comprising a copper component, an amine component, and a weak acid component.

In accordance with a third aspect of the present invention, there is provided a hydrometallurgical flotation process comprising the step of adding an activator to an ore slurry to be subjected to froth flotation, wherein the activator comprises a copper component, an amine component, and a weak acid component.
DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, there is provided an aqueous copper composition for use in hydrometallurgical flotation processes comprising a copper component, ammonium hydroxide or an amine component, and a weak acid component.

The copper component is preferably a water-soluble cupric salt, particularly copper sulphate, copper chloride, copper carbonate, and copper nitrate. Typically the copper component is present in an amount from 25 to 45 % (w/w).

The weak acid component is an organic carboxylic acid, preferably citric acid, tartaric acid, or oxalic acid. Useful weak acid components also include acetic acid, adipic acid, succinic acid or sulphamic acid. The weak acid component in the aqueous copper composition of the present invention serves as a buffering agent. Preferably, the weak acid component also behaves as a chelating agent. Typically the weak acid component is present in an amount from 3 to 15 % (w/w).

Ammonium hydroxide comprised in the aqueous copper composition of the present invention is derived from ammonium hydroxide solution (25 % NH₃). Typically the ammonium hydroxide solution is present in an amount from 20 to 45 % (w/w).

The amine component in the aqueous copper composition of the present invention is selected from a group comprising an amine of the general formula RNH₂, R₂NH, or R₃N, wherein R is an alky or aryl group, linear polyamines, branched polyamines, cyclic polyamines, aromatic heterocyclic amines or aliphatic heterocyclic amines. Preferably, the amine component is a water soluble alkyl amine. Useful amine ligands include ethanolamine, triethanolamine, trimethylamine, triethylamine, and hydroxylamine. Typically the amine component is present in an amount from 20 to 45 % (w/w).
In a preferred embodiment of the invention, the aqueous copper composition according to the present invention comprises 35 - 45 % (w/w) of copper sulphate, 35 - 45 % (w/w) of ammonium hydroxide solution (25 % NH₃), and 3 - 12 % (w/w) of citric acid.

Typically the aqueous copper composition of the present invention has a pH from 7.5 to 11, and a specific gravity of about 1.3.

It is envisaged that the aqueous copper composition of the present invention will be used as an activator, typically for the activation of sphalerite, pyrrhotite, marmatite and arsenopyrite, in a hydrometallurgical flotation process as a substitute for copper sulphate. Preferably, the aqueous copper composition is added in an amount in the range from 20 to 40 % (w/w) of the amount of copper sulphate usually added.

The aqueous copper composition of the present invention is arranged to be supplied as a concentrated solution that allows direct dosing of the composition to a hydrometallurgical process batch job. Alternatively, the composition can be batch diluted prior to dosing or diluted in line after a dosing pump. One kilogram of aqueous copper composition of the present invention provides a substantially equivalent concentration of copper ions for hydrometallurgical processes as 3.85 kg of copper sulphate.

The aqueous copper composition of the present invention is stable with regard to precipitation of copper hydroxide over pH range 0-11. Approximately 80 % of copper ions present in solution are available for adsorption onto mineral surfaces, making the composition many times more efficient than aqueous solutions of copper sulphate.

An additional advantage of the composition of the present invention over aqueous solutions of copper sulphate is that no adjustment to slurry pH is required after...
addition of the composition to a hydrometallurgical batch process, resulting in reduced consumption of lime. Lime is generally added to the slurry to adjust pH. This advantage results in shorter conditioning times and improved plant throughput. The present invention will now be described in further detail, by way of example only, in the following examples and figures wherein:

Figure 1 illustrates a gold grade-recovery curve resulting from comparative tests of the performance of copper sulphate and the aqueous copper composition (CUA 385) according to the present invention when used as an activator in a laboratory batch flotation test conducted on a reference ore (2.62 g/t Au and 1.03 % S);

Figure 2 illustrates a sulfur grade-recovery curve resulting from comparative tests of the performance of copper sulphate and the aqueous copper composition (CUA 385) of the present invention when used as an activator in a laboratory batch flotation test conducted on a reference ore (2.62 g/t Au and 1.03 % S);

Figure 3 illustrates rate of gold recovery resulting from comparative tests of the performance of copper sulphate and the aqueous copper composition (CUA 385) of the present invention when used as an activator in a laboratory batch flotation test conducted on a reference ore (2.62 g/t Au and 1.03 % S);

Figure 4 illustrates rate of sulfur recovery resulting from comparative tests of the performance of copper sulphate and the aqueous copper composition of the present invention (CUA 385), when used as an activator in a laboratory batch flotation test conducted on a reference ore (2.62 g/t Au and 1.03 % S); and

Figure 5 illustrates zinc grade/recovery curves for zinc rougher flotation tests conducted on lead scavenger tailing examining the impact of the aqueous copper composition of the present invention (Minplex), added at 150, 175, 200, and 225 grams per tonne, on sphalerite flotation.
EXAMPLES

Example 1
An aqueous copper composition was prepared by dissolving copper sulfate (250 kg) in water (200 L), followed by addition of ammonium hydroxide solution (25% NH₃) (250 L). A second addition of copper sulphate (250 kg) was made to the solution followed by a second addition of ammonium hydroxide solution (25% NH₃) (200 L). The composition was stirred until all components were fully dissolved. Citric acid (140kg) was added to the composition and stirred for 10 minutes. A third addition of ammonium hydroxide solution (25% NH₃) (50 L) was made and the composition was stirred for a further 10 minutes. The composition was then allowed to stand to enable contaminants to settle, and the resulting composition was decanted and packaged. The aqueous copper composition is a dark blue liquid, with a specific gravity of 1.3 and a solution pH of 8.

Example 2
An aqueous copper composition was prepared by treating a solution of copper carbonate (25 g) in water (30 mL) with tartaric acid (14.5 g) followed by ammonium hydroxide solution (25% NH₃) (8 g), whereupon a green suspension was obtained. A second addition of tartaric acid (14.5 g) was made to the suspension, followed by a second addition of ammonium hydroxide solution (25% NH₃) to adjust the pH of the solution to 10.5 - 11. The product obtained was dark blue in colour and was soluble in water.

Example 3
An aqueous copper composition was prepared by treating a solution of copper carbonate (25 g) in water (30 mL) with citric acid (9 g) followed by ammonium hydroxide solution (25% NH₃) (8 g), whereupon a green suspension was obtained. A
second addition of citric acid (8.5 g) was made to the suspension, followed by a
second addition of ammonium hydroxide solution (25% NH₃) to adjust the pH of the
solution to 9.8. The product obtained was dark blue in colour and was soluble in
water.

Example 4
An aqueous copper composition was prepared by treating a solution of copper
carbonate (25 g) in water (30 mL) with oxalic acid (13.5 g) followed by ammonium
hydroxide solution (25% NH₃) (8 g), whereupon a green suspension was obtained. A
second addition of oxalic acid (12.5 g) was made to the suspension, followed by a
second addition of ammonium hydroxide solution (25% NH₃) to adjust the pH of the
solution to 10.8. The product obtained was dark blue in colour and was soluble in
water.

Example 5
Cupric chloride (25 g) was suspended in water (30 mL). This mixture was treated
with ammonium hydroxide solution (25% NH₃) (16 g) whereupon a bluish-green
precipitate was obtained. The pH of the solution was 5.5 - 6.5. Citric acid (8.5 g) was
then added to the solution to reduce the pH to 4.0 - 5.0. A second portion of
ammonium hydroxide solution (25% NH₃) was added to the mixture to obtain a deep
blue solution with a pH of 8. The solution was soluble in water with no sediments.

Example 6
Cupric chloride (25 g) was suspended in water (30 mL). This mixture was treated
with ammonium hydroxide solution (25% NH₃) (16 g) whereupon a bluish-green
precipitate was obtained. The pH of the solution was 5.5 - 6.5. Tartaric acid (12.5 g)
was then added to the solution to reduce the pH to 4.0 - 5.0. A second portion of
ammonium hydroxide solution (25% NH₃) was added to the mixture to obtain a deep blue solution with a pH of 9.2. The solution was soluble in water with no sediments.

**Example 7**

5 Cupric sulphate (25 g) was suspended in water (9.5 mL). Ammonium hydroxide solution (25% NH₃) was added to the mixture until a pH of 7.5 was obtained. Tartaric acid (8.5 g) was then added to the mixture, whereupon the pH changed to 5.5 accompanied by an evolution of heat. The mixture was kept in a water bath and a second amount of ammonium hydroxide solution (25% NH₃) was added until a dark blue solution of pH 8.5 was obtained.

**Example 8**

Cupric sulphate (100 g) was suspended in water (88 mL). Triethanolamine (85 g) was added to the stirred suspension. Citric acid (33 g) was then added to the mixture.

15 After stirring for 15 minutes a second portion of triethanolamine (92 g) was added to provide a dark blue solution. The solution had a pH of 8.2, a specific gravity of 1.3, and it was freely soluble in water.

**Example 9**

20 Cupric sulphate (100 g) was suspended in water (88 mL). Ethanolamine (55 g) was added to the stirred suspension. Citric acid (33 g) was then added to the mixture. After stirring for 15 minutes a second portion of ethanolamine (35 g) was added to provide a dark blue solution. The solution had a pH of 7.8, a specific gravity of 1.3, and it was freely soluble in water.

**Example 10**

A standard laboratory batch flotation test was carried out in a 5 L Agitair laboratory flotation cell. A reference ore was prepared by grinding to a P₈₀ of 150 μm in a
laboratory rod mill with process water. The resultant slurry density was made up to 35 % solids (w/w). Head grade of the reference ore was 2.62 g/t Au and 1.03 % S. Comparative tests in relation to the performance of the aqueous copper composition of the present invention as an activator compared with copper sulphate were conducted. Copper sulphate was added to the slurry at 20 g/t, whereas the aqueous copper composition was added at 7 g/t. After addition of the activator the slurry was conditioned for one minute. Standard PAX was then added to the mixture at 6 g/t with a further one minute conditioning. Two to three drops of frother (ISO) were then added, air was introduced to the cell, and concentrate samples were removed after a one minute period, a three minute period, and a six minute period from addition of the frother. The concentrates and final tailings weights were recorded and gold and sulphur assays were conducted thereon.

Referring to Figures 1 and 2, it is evident that a higher cumulative gold recovery is afforded in all three concentrates when the aqueous copper composition of the present invention is used as an activator in comparison to copper sulphate. The grade-recovery curve for sulphur also shows improvement in both grade and recovery over the copper sulphate activator. Although the final grades are similar for both reagents, the recovery difference is in the order of 20 % in favour of the aqueous copper composition as activator.

Figures 3 and 4 illustrate a distinct improvement in the initial rates of gold and sulphur recovery when the aqueous copper composition is used as the activator rather than copper sulphate.

Example 1

Laboratory zinc rougher flotation tests were completed on lead scavenger tailings wherein the performance of the aqueous copper composition of the present invention
as an activator was compared with the performance of copper sulphate (500 grams per
tonne of copper sulphate. Zinc rougher flotation tests were completed at 150, 175,
200, and 225 grams per tonne of the aqueous copper composition. The zinc
grade/recovery curves are displayed in Figure 5. Table 1 contains the zinc and iron
grades of the zinc concentrate, and the diluent recoveries at 60 percent zinc recovery.

It is evident from Figure 5 that the zinc grade/recovery is enhanced when the aqueous
copper composition of the present invention is used as an activator in comparison with
copper sulphate. At 60 percent zinc recovery the zinc concentrate grade was
increased from 34.8 percent for the standard test to 48.6 percent for the test conducted
at 175 grams per tonne of the aqueous copper composition. The improvement in zinc
concentrate grade was due to better selectivity for sphalerite against lead, iron
sulphides (IS) and non-sulphide gangue (NSG).

Similar tests on lead scavenger tailing from other mine sites revealed that optimum
zinc recovery and concentrate grade is achieved when the aqueous copper
composition is added in an amount in the range from 20 to 40 % (w/w) of the amount
of copper sulphate usually added. The data suggests that addition of the aqueous
copper composition at the optimum rate produced the same or better metallurgy when
compared with copper sulphate. The composition resulted in either an improved zinc
concentrate grade at the specified zinc recovery or and increase in zinc recovery at the
specific zinc concentrate grade.

Use of the composition also results in an increase in the ore pulp pH, compared with a
decrease when copper sulphate was used.
Table 1: Zinc and iron grades of the zinc concentrate and diluent recoveries, at 60% zinc recovery, for zinc rougher flotation tests conducted on lead scavenger tailing.

<table>
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<tr>
<th>Test Description</th>
<th>Grade, %</th>
<th>Diluent recovery, %</th>
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<tbody>
<tr>
<td></td>
<td>Zn</td>
<td>Fe</td>
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<tr>
<td>500g/t CuSO₄</td>
<td>34.84</td>
<td>9.39</td>
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<tr>
<td>150g/t Minplex</td>
<td>47.88</td>
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<td>175 g/t Minplex</td>
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<td>200g/t Minplex</td>
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<tr>
<td>225 g/t Minplex</td>
<td>44.00</td>
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5 Modifications and variations as would be apparent to a skilled addressee are deemed to be within the scope of the present invention.
CLAIMS

1. An aqueous copper composition for use in hydrometallurgical flotation processes comprising a copper component, ammonium hydroxide, and a weak acid.

2. An aqueous copper composition for use in hydrometallurgical flotation processes comprising a copper component, an amine component, and a weak acid.

3. The composition according to claim 2, characterised in that the amine component is an amine selected from a group comprising amines of the general formula RNH₂, R₂NH, or R₃N, wherein R is an alky or aryl group, linear polyamines, branched polyamines, cyclic polyamines, aromatic heterocyclic amines and aliphatic heterocyclic amines.

4. The composition according to claim 3, characterised in that the amine is a water soluble alkyl amine.

5. The composition according to claim 3 or claim 4, characterised in that the amine is ethanolamine, triethanolamine, trimethylamine, triethylamine, or hydroxylamine.

6. The composition according to claim 5, characterised in that the amine is ethanolamine.

7. The composition according to claim 5, characterised in that the amine is triethanolamine.

8. The composition according to any one of claims 2 to 7, characterised in that the amine component is present in an amount from 20 to 45 % (w/w).

9. The composition according to any one of claims 1 to 8, characterised in that the copper component is a water soluble cupric salt.
10. The composition according to claim 9, characterised in that the cupric salt is copper sulphate, copper chloride, copper carbonate, or copper nitrate.

11. The composition according to any one of claims 1 to 10, characterised in that the copper component is present in an amount from 25 to 45 % (w/w).

12. The composition according to any one of claims 1 to 11, characterised in that the weak acid component is an organic carboxylic acid.

13. The composition according to any one of claims 1 to 12, characterised in that the weak acid component is citric acid, tartaric acid, oxalic acid, acetic acid, adipic acid, succinic acid, or sulphamic acid.

14. The composition according to any one of claims 1 to 13, characterised in that the weak acid component serves as a buffering agent.

15. The composition according to any one of claims 1 to 14, characterised in that the weak acid component is a chelating agent.

16. The composition according to any one of claims 1 to 15, characterised in that the weak acid component is present in an amount from 3 to 15 % (w/w).

17. The composition according to any one of claims 1 to 16, characterised in that ammonium hydroxide comprised in the aqueous copper composition is derived from ammonium hydroxide solution (25 % NH₃).

18. The composition according to any one of claims 1 to 17, characterised in that the ammonium hydroxide component is present in an amount from 20 to 45 % (w/w).

19. The composition according to any one of claims 13 to 18, characterised in that the composition comprises from 35 to 45 % (w/w) of copper sulphate, from 35 to 45 % (w/w) of ammonium hydroxide solution (25 % NH₃), and from 3 to 12 % (w/w) of citric acid.
20. The composition according to any one of claims 1 to 19, characterised in that the composition has a pH from 7.5 to 11, and a specific gravity of about 1.3.

21. Use of the aqueous copper composition according to any one of claims 1 to 20 as an activator in a hydrometallurgical flotation process.

22. Use of the aqueous copper composition according to any one of claims 1 to 20 for activation of sphalerite, pyrrhotite, marmatite and arsenopyrite in a hydrometallurgical flotation process.

23. Use of the composition according to claim 21 or claim 22, characterised in that dosage of the composition is in the range from 20 to 40 % (w/w) of standard dosage of copper sulphate.

24. A hydrometallurgical flotation process comprising the step of adding an activator to an ore slurry to be subjected to froth flotation, wherein the activator comprises the aqueous copper composition according to any one of claims 1 to 20.

25. The process according to claim 24, characterised in that the activator is added in an amount from 20 to 40 % (w/w) of the standard amount of copper sulphate added.
Figure 1. Gold grade-recovery curves for copper sulphate and CUA 385

Figure 2. Sulphur grade-recovery curves for copper sulphate and CUA 385
Figure 3. Rate of gold recovery

Figure 4. Rate of sulphur recovery
Figure 5. Zinc grade/recovery curves for zinc rougher flotation tests conducted on lead scavenger tailings examining the impact of Minplex (at 150, 175, 200, 225 grams per tonne) on sphalerite flotation.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.: B03B 1/00, B03D 1/002, 1/018, 1/01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC B03B 1/00, B03D 1/002, 1/018, 1/01

Documentation: searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI IPC + KEYWORDS (COPPER CUPRIC, AMINE, ACID)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>Derwent Abstract Accession No.90-065492/09, Class E19, SU 1477783 A, (ODESS POLY) 7 May 1989</td>
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Further documents are listed in the continuation of Box C

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  "O" document referring to an oral disclosure, use, exhibition or other means
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  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  "X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  "&" document member of the same patent family

Date of the actual completion of the international search
7 November 2001

Date of mailing of the international search report
15 NOV 2001

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Form PCT/ISA/210 (second sheet) (July 1998)
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<td>US 5328561 A (LETIZE et al.) 12 July 1994</td>
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This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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